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# **ATMOSPHERIC TRANSFORMATION OF VOLATILE ORGANIC COMPOUNDS**

**Michael V. Henley, Gina M. Graziano, J. Raymond Wells**  
**Air Force Research Laboratory**

**William R. Bradley, Sheryl E. Wyatt (Calidonna)**  
**Applied Research Associates**  
**P.O. Box 40128**  
**Tyndall AFB, FL 32403**

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# Atmospheric transformation of volatile organic compounds

M.V. Henley<sup>\*a</sup>, W.R. Bradley<sup>b</sup>, Sheryl E. Wyatt<sup>b</sup>, G.M. Graziano<sup>a</sup> and J.R. Wells<sup>c</sup>

<sup>a</sup>Air Force Research Laboratory/MLQL, Tyndall AFB, FL 32403

<sup>b</sup>Applied Research Associates, Tyndall AFB, FL 32403

<sup>c</sup>NIOSH, Morgantown, WV 26505

## ABSTRACT

To be able to understand and predict the concentration of a target compound in the atmosphere one must understand the atmospheric chemistry involved. The transformation of volatile organic compounds (VOCs) in the troposphere is predominantly driven by the interaction with the hydroxyl and nitrate radicals. The hydroxyl radical exists in daylight conditions and its reaction rate constant with an organic compound is typically very fast. The nitrate radical drives the nighttime chemistry. These radicals can scavenge hydrogen from an organic molecule generating secondary products that are often overlooked in detection schemes. Secondary products can be more stable and serve as a better target compound in detection schemes. The gas phase reaction of the hydroxyl radical (OH) with cyclohexanol (COL) has been studied. The rate coefficient was determined to be  $(19.0 \pm 4.8) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (at  $297 \pm 3 \text{ K}$  and 1 atmosphere total pressure) using the relative rate technique with pentanal, decane, and tridecane as the reference compounds. Assuming an average OH concentration of  $1 \times 10^6 \text{ molecules cm}^{-3}$ , an atmospheric lifetime of 15 h is calculated for cyclohexanol. Products of the OH + COL reaction were determined to more clearly define cyclohexanol's atmospheric degradation mechanism. The observed products were: cyclohexanone, hexanedial, 3-hydroxycyclohexanone, and 4-hydroxycyclohexanone. Consideration of the potential reaction pathways suggests that each of these products is formed via hydrogen abstraction at a different site on the cyclohexanol ring.

Keywords: OH, hydroxyl radical rate constant, cyclohexanol, reaction products, atmospheric chemistry

## 1. INTRODUCTION

To be able to understand and predict the concentration of a target compound in the atmosphere one must understand the atmospheric chemistry involved. The transformation of volatile organic compounds (VOCs) in the troposphere is predominantly driven by interaction with the hydroxyl and nitrate radicals. The hydroxyl radical exists in daylight conditions and its reaction rate constant with an organic compound is typically very fast. The nitrate radical drives the nighttime chemistry. These radicals can scavenge hydrogen from an organic molecule generating secondary products that are often overlooked in detection schemes. Secondary products can be more stable and serve as better target compounds in detection schemes.

There are two fundamental questions that must be answered in order to be able to understand and predict the fate of a volatile organic compound in the atmosphere. These questions are "How quickly does it react?" and "What are its transformation pathways and products?" To answer these questions for the daytime reaction of hydroxyl radical with a volatile organic compound, a series of experiments is conducted to determine the kinetic rate constant and any reaction products produced. From the experimental data an atmospheric lifetime can be calculated and transformation pathways proposed.

\* Correspondence: Email: [mike.henley@tyndall.af.mil](mailto:mike.henley@tyndall.af.mil); Telephone: 850-283-6050; Fax: 850-283-6090

We have previously reported the results from studies of the gas-phase reactions of several oxygenated organic species<sup>1-6</sup> and siloxanes<sup>7</sup> with the hydroxyl radical (OH). In the current work, we investigate the gas-phase reactions of cyclohexanol with OH, present its kinetic and product data, and make comparisons with predicted data using structure-activity relationships [SAR].<sup>8</sup> Cyclohexanol is an important industrial precursor in the production of other ringed species<sup>9</sup> and its emission during these processes is sure to occur. The day and nighttime reactions that occur in the troposphere impact detection of its release. This study focuses on its daytime chemistry.

In the troposphere, most volatile saturated organic compounds have been shown to react with OH via hydrogen abstraction to form alkoxy radicals (RO)<sup>10</sup>. Cyclohexanol, for example, has four unique sites for potential hydrogen removal as shown in Scheme 1.

The overall rate of the OH + COL reaction is dependent upon the reaction rate at each abstraction site. The relative contribution from each site and the subsequent reactions of the radicals formed (the reaction channel) determine the quantitative mix of degradation products. In Scheme 1, we also depict the expected subsequent reactions of each cyclohexoxy alkoxy radical. Some subsequent reaction pathways are omitted based on estimation of the relative importance of the reactions of certain alkoxy radicals<sup>10-11</sup>. In this paper, we report the overall rate constant of OH with cyclohexanol as measured by the relative rate method<sup>12</sup>. The observed products of the OH + COL reaction in the presence of NO are reported and used to assess cyclohexanol's expected atmospheric reaction mechanism. Neither the OH rate constant nor possible reaction mechanisms for cyclohexanol have been reported previously.

## 2. EXPERIMENTAL

### 2.1. Reaction chamber

Kinetic and product determination experiments were conducted with apparatus similar to previous studies<sup>1,3,13,14</sup>. A brief description is provided here. Reactants were introduced and samples were withdrawn through a 6.4-mm Swagelok fitting attached to a 2-mil FEP Teflon<sup>®</sup>-film bag (50 - 120 L). Dry compressed air was added as a diluent to the reaction bag and measured with a 0-100 L·min<sup>-1</sup> MKS mass flow controller. The filler system was equipped with a syringe injection port facilitating the introduction of both liquid and gaseous reactants via the flowing airstream. All reactant mixtures and calibration standards were generated by this system. Irradiation was carried out by placing the reaction bag into a light tight chamber. The chamber employed the following mix of lamps: 6-Philips TL40W/03; 1-GE F40BL; 2-QPANEL UV351 and 7-QPANEL UV340. This lamp mixture approximates solar radiation from 300 to 450 nm.

### 2.2. Kinetic Rate Method

The experimental procedures for determining the OH + COL reaction kinetics were similar to those described previously<sup>13,14</sup>.

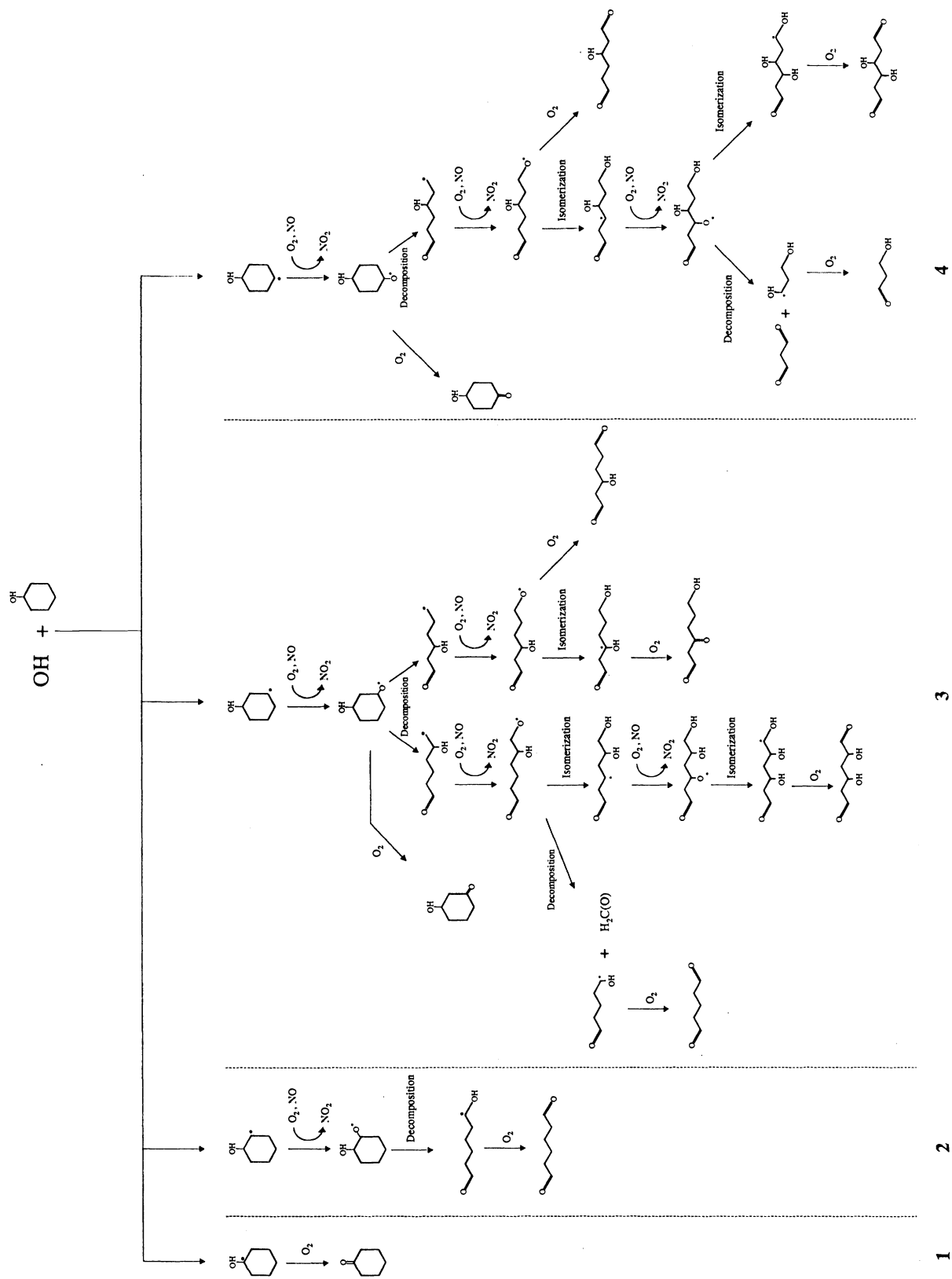


The rate equations for reactions 1 and 2 are combined and integrated resulting in the following equation:

$$\ln \left( \frac{[\text{COL}]_0}{[\text{COL}]_t} \right) = \frac{k_{\text{COL}}}{k_{R_j}} \ln \left( \frac{[\text{R}_j]_0}{[\text{R}_j]_t} \right) \quad (I)$$

If reaction with OH is the only removal mechanism for cyclohexanol and reference, a plot of  $\ln([\text{COL}]_0/[\text{COL}]_t)$  versus  $\ln([\text{R}_j]_0/[\text{R}_j]_t) / k_{R_j}$  yields a straight line with an intercept of zero and a slope equal to  $k_{\text{COL}}$ . The OH rate constant experiments for cyclohexanol employed the use of three reference compounds ( $\text{R}_j$ ), decane, tridecane, and pentanal. The use of three different reference compounds with different OH rate constants increases the confidence in the validity of the OH + COL rate constant measured.

**Scheme 1.**



Nitric oxide (NO, 99%+ pure obtained from Matheson Gases) was added to facilitate the generation of OH and to minimize ozone (O<sub>3</sub>) and NO<sub>3</sub> formation. Thus the experimental parameters would favor the first OH hydrogen abstraction step with minimal opportunity for side reactions from other radicals.

The typical concentrations of the pertinent species in the reaction bag were 1.4-3.5 ppm cyclohexanol, 1.2-2.8 ppm reference, 10 ppm CH<sub>3</sub>ONO, and 1 ppm NO in air. These mixtures were allowed to stand for 30-60 minutes before initial species concentration ([X]<sub>0</sub>) samples were collected. Typically, stepped 3-5 second irradiation intervals were used on the reaction mixture for a combined total photolysis time of approximately 50 seconds.

### 2.3. Kinetic Study Analysis

Samples from kinetic studies were quantitatively monitored using a Hewlett-Packard (HP) gas chromatograph (GC) 5890 with a flame ionization detector (FID) or a Mass Selective Detector (MSD) using HP series Chem Station software. The FID signal or total ion chromatogram (TIC) was used to determine cyclohexanol and reference concentrations. Gas samples for both detectors were cryogenically (-65°C) collected on a Hastelloy C sample loop (~1.3 ml) and injected onto the GC column (Restek Stabilwax-DA, 0.53 mm i.d., 30-m, 1.0 µm film thickness) with a heated rotary valve<sup>15</sup>. The GC temperature program used was as follows: 45°C for 10 minutes then 12°C/min to 220°C and held for 3 minutes. Helium (UHP grade), the carrier gas, was supplied by Air Products and used as received.

All measurements were at least duplicated. A relative standard deviation (the data set standard deviation divided by the data set average) of approximately 2.5% was achieved with the described sampling method. Several interference experiments were conducted to assure the validity of the OH rate constant. They consisted of looking for possible chromatographic co-elution of methyl nitrite, NO, reference, cyclohexanol and the hydroxyl radical reaction products. Two control experiments were conducted to determine the stability of the reference and cyclohexanol coexisting in the same bag. First the reference and cyclohexanol were injected into the bag, quantified, photolyzed for 6 minutes and re-quantified. Second methyl nitrite, NO, reference and cyclohexanol were injected into the bag, quantified, left in the bag overnight and then re-quantified. None of these preliminary experiments yielded chromatographic peak overlaps or observable reactions occurring without photoinitiation. At the end of each run, the Teflon<sup>®</sup> bag was cleaned by flushing the bag 6 times with air containing <0.1 ppm total hydrocarbon. Measurements of an air filled bag showed no cross contamination between runs.

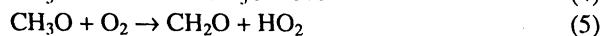
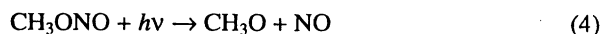
### 2.4. Product Study Analysis

Reactant mixtures and standards from product identification experiments were sampled by exposing a 100% polydimethylsiloxane solid phase microextraction fiber (SPME, Supelco) in the reaction bag for 2 minutes. SPME samples were subsequently analyzed with a ThermoQuest Trace 2000 GC combined with a Finnigan GCQ mass spectrometer. Full scan electron impact ionization spectra were collected from 29 to 250 mass units. The TIC was used to determine cyclohexanol and product concentrations. A Restek Rtx-1701 column (0.53 mm i.d., 30-m length, 1.0 µm film thickness) provided compound separation. The GC temperature program used was as follows: 35°C for 5 minutes then 6°C/min to 125°C and held for 11 minutes. Helium (UHP grade), the carrier gas, was supplied by Air Products and used as received.

Analysis for carbonyl compounds produced by gas-phase reactions were conducted by flowing 10 L of the reaction bag contents over 2,4-dinitrophenylhydrazine (DNPH) impregnated cartridges. Hydrazones formed by derivatization were extracted with acetonitrile and quantitatively measured by HPLC (HP 1050) using a three component gradient solvent program as described previously<sup>16</sup>.

### 2.5. Chemicals and Reagents

OH, the primary oxidizing radical in the atmosphere, was generated from the photolysis of methyl nitrite (CH<sub>3</sub>ONO) in the presence of nitric oxide (NO) in air<sup>12</sup>.



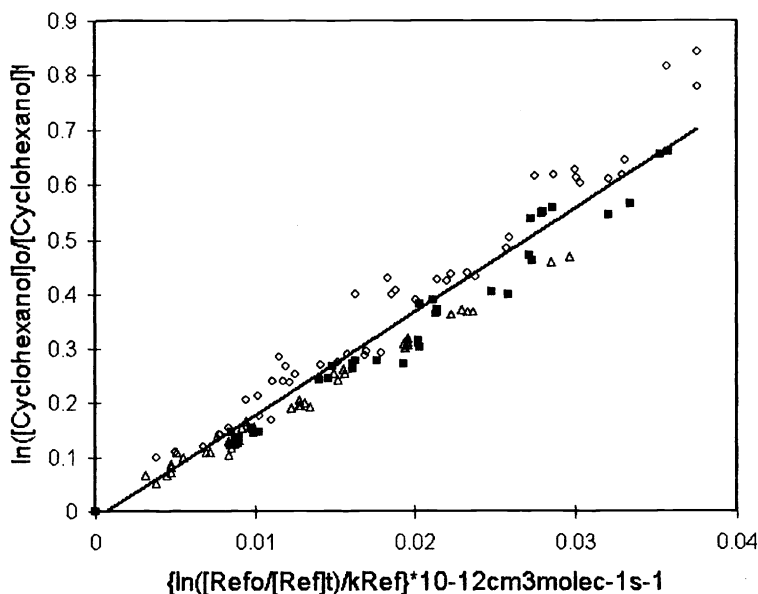
CH<sub>3</sub>ONO was prepared in gram quantities using the method of Taylor *et al.*<sup>17</sup> and stored in a lecture bottle at room temperature. The CH<sub>3</sub>ONO purity (>95%) was verified by FT-IR.

All volatile organic compounds were used as received. cyclohexanol, tridecane, and decane were obtained from Aldrich with a purity of 99%+. Pentanal (99%+) and cyclohexanone (99%+) were purchased through Ultra Scientific. Methanol and acetonitrile, HPLC grade, were received from Aldrich Chemical. The water was distilled, deionized to 18 megaohm, and filtered using a Milli-Q® filter system. Experiments were carried out at 298 ± 3 K at about 1 atmosphere.

### 3. RESULTS

#### 3.1. OH + COL Reaction Rate Constant ( $k_{COL}$ )

Typically five experimental runs were conducted on each COL/reference pair. The plot of a modified version of equation (I) is shown in Figure 1.



**Figure 1.** COL relative rate plot with decane (O), pentanal ( $\Delta$ ) and tridecane ( $\blacksquare$ ) as reference compounds. The OH + COL rate constant,  $k_{COL}$ , measured is  $19.0 \pm 0.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

The  $\ln([R_i]_0/[R_i]_t)$  term is divided by the respective reference rate constant (decane  $11.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , tridecane  $16 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and pentanal  $28.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )<sup>10</sup> and multiplied by  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  resulting in a unitless number. This yields a slope that is equal to the hydroxyl radical/COL rate constant,  $k_{COL}$ , divided by  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This modification allows for a direct comparison of the three reference compound/COL data sets.

The combined data results in a slope that yields a hydroxyl radical bimolecular rate constant,  $k_{COL}$ , of  $(19.0 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The data points at the origin are experimental points because pre-irradiation,  $t = 0$ , data showed no detectable loss of cyclohexanol or reference. The error in the rate constant stated above is the 95% confidence level from the random uncertainty in the slope. Analysis of the calculated y-intercept show the value to be not statistically different than zero (95% confidence level). Incorporating the uncertainties associated with the reference rate constants ( $\pm 25\%$ ) used to derive  $k_{COL}$ , yields a final value of  $(19.0 \pm 4.8) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Assuming an  $[\text{OH}] = 1 \times 10^6 \text{ molecules cm}^{-3}$ , the atmospheric (1/e) lifetime calculated for cyclohexanol is 15 hours. The observed rate constant can be compared with  $k_{COL} = 17.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , calculated using SAR relationships<sup>8</sup> programmed into the Atmospheric Oxidation Program (AOPWIN v1.89) available from Syracuse Research Corporation. This estimated value is within the error limits of the final value reported here.

### 3.2. Identification of OH + COL Reaction Products

Cyclohexanone (CON) was the only OH + COL reaction product observed during the initial kinetic experiments. Its presence was also detected later using the DNPH derivatization method described above and confirmed against a commercial standard. HPLC analysis of the DNPH cartridges also indicated at least one other carbonyl product in addition to cyclohexanone. The unknown product(s) eluted closely to cyclohexanone indicating similar size. An intermediate polarity column (Rtx-1701) was selected for further analysis in the system used for kinetic experiments (conditions similar to those ultimately used for the GCQ). Traces of hexanedial (HxD), 3-hydroxycyclohexanone (3HC), and 4-hydroxycyclohexanone (4HC) were detected, but quantitative results were not repeatable (>30%). However, there was sufficient data to allow preliminary compound identifications from the mass spectral data sets by searching the Wiley/NBS Mass Spectra Library. It was thought that the quantitative problems arose from the cryogenic trapping system, so sampling via SPME fiber was substituted. SPME samples were analyzed on the GCQ and the repeatability found to be acceptable (<5%). Identification of each isomer was achieved by comparing the spectral and retention time data of the GCQ to that of the GC/MSD (commercial standards of the isomers were not readily available to allow direct confirmation).

Typically, oxygenated organic species react with OH to subsequently generate other oxygenated organic products<sup>1-6,11,18-22</sup>. The reaction products cyclohexanone, hexanedial, 3-hydroxycyclohexanone, and 4-hydroxycyclohexanone are therefore consistent with previously observed products from OH + oxygenated organic species.

## 4. DISCUSSION

The results presented demonstrate the importance of understanding the atmospheric chemistry that occurs with volatile organic compounds. We have shown that the reactivity of cyclohexanol with OH in the troposphere will quickly impact its expected atmospheric concentrations. Cyclohexanone reacts with OH to produce four primary products cyclohexanone, hexanedial, 3-hydroxycyclohexanone, and 4-hydroxycyclohexanone. These products can subsequently react with additional OH to generate secondary products. These experiments were designed to limit the formation of secondary products and therefore they were not observed. The most abundant product, cyclohexanone, has a reported experimental OH rate constant of  $6.39 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ <sup>123</sup>. Expressed in an atmospheric lifetime (1/e), this corresponds to approximately 43 hours as compared to 15 hours for cyclohexanol. This indicates that in a detection scheme cyclohexanone could serve as a better target.

The proposed mechanism for the formation of cyclohexanone, the principal product observed from the OH + COL reaction, has the radical generated by site 1 abstraction reacting with O<sub>2</sub> to form cyclohexanone rather than forming an RO<sup>•</sup> intermediate (see Scheme 1). This mechanism is consistent with previously reported mechanisms for hydroxyl radical reactions with alcohols<sup>3</sup>. The calculated rate constant (AOPWIN v1.89) for site 1 is  $k = 10.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , whereas the rates for sites 2-4 are each  $k = 1.41 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The faster reaction rate for site 1 is predicted based on it having the hydroxyl group attached, making it more reactive. The hydrogens at sites 2, 3, and 4 are attached to secondary carbons and therefore do contribute significantly to the overall rate. Still, much lower abstraction rates for these sites are predicted because they have no groups attached directly or on the next nearest neighbor which enhance their respective hydroxyl reactivities.

Subsequent reactions of the RO<sup>•</sup> radicals formed at sites 2-4 can include reaction with O<sub>2</sub>, unimolecular decomposition, and isomerization<sup>10,11</sup>. Previous studies have indicated that isomerization reactions of cyclohexoxy radicals are of minor or negligible importance because of the preferred chair conformation<sup>18</sup>. The position of the OH group relative to the radical at sites 2-4 largely determines the likelihood of oxidation or decomposition as well as the further degradation of cyclohexanol.

Previous work with β-hydroxyalkoxy radicals (as formed by hydrogen abstraction at Site 2) have indicated that for this class of compounds, decomposition is generally more significant than oxidation<sup>11</sup>. This is particularly true when the radical leaving species has more than one carbon. For example, for the CH<sub>2</sub>CH(OH)CH(O<sup>•</sup>)CH<sub>3</sub> radical, the calculated  $k_d = 2.7 \times 10^7 \text{ s}^{-1}$  versus a calculated  $k_{O_2}[O_2] = 4.1 \times 10^4 \text{ s}^{-1}$ <sup>111</sup>. The predominance of decomposition is in agreement with the observance of only the product hexanedial from reaction site 2.

Both decomposition and oxidation should be significant pathways for the alkoxy radicals formed from abstraction at sites 3 and 4. For example, Atkinson et al., reports for the cyclohexoxy radical, the calculated  $k_d = 6.3 \times 10^4 \text{ s}^{-1}$  and  $k_{O_2}[O_2] = 2.2 \times 10^4 \text{ s}^{-1}$ <sup>118</sup>. The products observed in this study, 3-hydroxycyclohexanone and 4-hydroxycyclohexanone, are indicative of only the oxidation pathway. However, it can be seen from Scheme 1 that decomposition pathways for both of these reaction



channels have multiple splits ultimately resulting in several very reactive species (see Table 1, several predicted  $k_{OH} > 70$ ). Therefore, the initial products from the decomposition paths may be present in concentrations beneath the detection limits of our current equipment. No secondary products of significant molecular weight were detected and attempts to monitor smaller species such as formaldehyde or carbon monoxide provide no conclusive insight as they are formed also during OH generation from methyl nitrite.

## 5. CONCLUSIONS

The OH + COL bimolecular rate constant,  $k_{COL}$ , was measured using the relative rate technique. A value for  $k_{COL}$  of  $(19.0 \pm 4.8) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was determined. Using [OH] of  $1 \times 10^6 \text{ molecules cm}^{-3}$  yields an atmospheric (1/e) lifetime for cyclohexanol of approximately 15 hours.

OH + COL reaction products cyclohexanone, hexanedial, 3-hydroxycyclohexanone, and 4-hydroxycyclohexanone were evaluated in light of the expected atmospheric reaction mechanisms. The mechanisms propose that the OH radical abstracts hydrogen from all four of the possible sites on cyclohexanol. The alcoholic hydrogen (site 1) is the most active site in agreement with SAR predictions<sup>8</sup>. The position of the OH group relative to the alkoxy radical determines the dominant subsequent reactions (isomerization, decomposition, or reaction with O<sub>2</sub>) for sites 2-4.

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